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MANUFACTURE OF AROMATIC CARBONIC ESTERS

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Abstract

Objective

To offer a method pertaining to the manufacture of aromatic carbonic ester by means of a reaction between aromatic hydroxy compound, carbon monoxide and oxygen, where aromatic carbonic esters can be manufactured at high yields using a catalyst system that is simpler than those of the past and can be recycled.

Constitution

A catalyst system is used that comprises (A) one or more types of substances selected from palladium and palladium compounds, (B) one or more types of compound containing cerium, cobalt or manganese metal ions as redox agent, (C) one or more types of inorganic halide selected from alkali metal halides and alkaline earth metal halides, and (D) activated carbon.

Claims

1. A method for manufacturing aromatic carbonic esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonic esters being characterized in that said reaction is carried out in a reaction system in the presence of (A) one or more types of substance selected from palladium and palladium compounds, (B) one or more types of compound containing

cerium, cobalt or manganese metal ions as redox agent, (C) one or more types of inorganic halide selected from among alkali metal halides and alkaline earth metal halides and (D) activated carbon.

2. The method according to Claim 1, wherein the aforementioned palladium compound is an organic acid salt of palladium.

3. The method according to Claim 1, wherein the aforementioned component (B) is a trivalent or tetravalent cerium compound, or divalent or trivalent cobalt or manganese.

4. The method according to Claim 1, wherein the aforementioned inorganic halide is a chloride or bromide.

5. The method according to Claim 1, wherein the aforementioned inorganic halide is cesium chloride or cesium bromide.

6. The method according to Claim 1, wherein the used amount of the aforementioned activated carbon is 20x or greater with respect to the palladium metal.

Detailed description of the invention

[0001]

Industrial field of the invention

The present invention concerns a method for the manufacture of aromatic carbonic esters using a special catalyst. Aromatic carbonic esters, particularly diphenyl carbonate, are useful as raw materials in the production of polycarbonate and other substances.

[0002]

Prior art

In the past, methods wherein an aromatic hydroxy compound and phosgene are allowed to react have been used as methods for manufacturing aromatic carbonic esters. However, these methods are undesirable due to the high toxicity of phosgene. Thus, a number of methods have been offered that do not use phosgene whereby aromatic carbonic esters are manufactured in a reaction between an aromatic hydroxy compound, carbon monoxide and oxygen.

[0003]

With regard to catalysts that are used in such methods, a method is described in Japanese Kokai Patent Application No. Sho 56[1981]-38144 wherein a palladium compound, a compound containing a metal from group IIIA, IVA, VA, VIA, IB, IIB, VIB or VIIB of the periodic table and a base are used; a method is described in Japanese Kokai Patent Application No. Sho 56[1981]-38145 wherein a palladium compound, manganese complex, cobalt complex, base and desiccant are used; a method is described in Japanese Kokai Patent Application No. Hei 1[1989]-165551 wherein a palladium compound, iodine compound and zeolites are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-104564 wherein a palladium compound, divalent or trivalent manganese compound, tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 2[1990]-142754 wherein a palladium compound, divalent or trivalent cobalt compound,

tetraalkylammonium halide and quinones are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-25095, wherein a palladium compound, cobalt compound, organic or inorganic halide and basic compound are used; a method is described in Japanese Kokai Patent Application No. Hei 5[1993]-58961, wherein a palladium compound, cobalt compound, and alkali metal halide are used; and a method is offered in Japanese Kokai Patent Application No. Hei 5[1993]-97775 wherein a palladium compound, inorganic auxiliary catalyst selected from cobalt, iron, cerium, manganese, molybdenum, samarium, vanadium, chrome and copper, an organic auxiliary catalyst selected from an aromatic ketone, aliphatic ketone or aromatic polycyclic hydrocarbon, and a quaternary ammonium salt are used.

[0004]

Problems to be solved by the invention

Conventional catalyst systems used in the manufacture of aromatic carbonic esters have had complicated reaction systems that require the use of quaternary ammonium salts, bases or organic auxiliary catalysts in order to increase the yield of target compound. For this reason, these catalysts have been complicated. Moreover, quaternary ammonium salts are particularly unstable under reaction conditions, and there have been problems with the production of large amounts of phenol bromide, for example. In addition, recycling of the catalyst is complicated. On the other hand, yields are low when these compounds are not used, and the methods become impractical. The objective of the present invention is thus to offer a method for manufacturing the

target aromatic carbonic esters at high yields using a catalytic system that is simple and can be recycled.

[0005]

Means to solve the problems

The inventors of the present invention et al. arrived at the present invention upon discovering that the aromatic carbonic esters can be produced with improved efficiency by using the special catalyst system described below. Specifically, the present invention is a method for manufacturing aromatic carbonate esters wherein an aromatic hydroxy compound is allowed to react with oxygen and carbon monoxide, said method for manufacturing aromatic carbonate esters being characterized in that said reaction is carried out in a reaction system in the presence of (A) one or more types of substance selected from palladium and palladium compounds, (B) one or more types of compound containing cerium, cobalt or manganese metal ions as redox agent, (C) one or more types of inorganic halides selected from among alkali metal halides and alkaline earth metal halides and (D) activated carbon.

[0006]

Specific description of the invention

1. Reaction raw materials

1) Aromatic hydroxy compound

The aromatic hydroxy compound that is used in the present invention is an aromatic mono- or polyhydroxy compound. Examples include phenol; cresol, xlenol, trimethylphenol, tetramethylphenol, ethylphenol, propylphenol, methoxyphenol, ethoxyphenol, chlorophenol, dichlorophenol, bromophenol, dibromophenol and other substituted phenols and isomers thereof; naphthol, methylnaphthol, ethylnaphthol, chloronaphthol, bromonaphthol and other substituted naphthols and isomers thereof; 2,2-bis(4-hydroxyphenyl)propane and various other types of bisphenols; various types of biphenols; various types of hetero-aromatic hydroxy compounds and isomers thereof; as well as compounds thereof produced by substitution with alkyl groups or halogen atoms. Of these compounds, phenol is particularly desirable.

[0007]

(2) Carbon monoxide

The carbon monoxide is gaseous state that is used in the present invention is produced by starting with a high-purity substance and mixing it with another gas that does not have a

detrimental influence on the reaction, such as nitrogen, argon, carbon dioxide or hydrogen.

[0008]

(3) Oxygen

The oxygen in gaseous state that is used in the present invention is produced by starting with a high-purity substance and mixing it with another gas that does not have a detrimental influence on the reaction, such as [atmospheric] air, nitrogen, argon, carbon dioxide or hydrogen.

[0009]

2. Catalyst

The catalyst that is used in the reaction of the present invention comprises the three components (A)-(D) below.

(A) Palladium or palladium compounds

The palladium and palladium compounds that are used in the present invention are palladium black; palladium carbon, palladium/alumina, palladium/silica or other carried palladium substances; palladium chloride, palladium bromide, palladium iodide, palladium sulfate, palladium nitrate or other inorganic palladium salts; and palladium acetate, palladium oxalate, palladium formate, palladium benzoate or other organic palladium acid salts. In addition, substances that can also be used include

palladium(II) acetylacetonate, palladium complexes produced by the coordination of carbon monoxide, nitriles, amines, phosphines or olefins on palladium, examples of which include $\text{PdCl}_2(\text{PhCN})_2$, $\text{PdCl}_2(\text{PPh}_3)_2$, $\text{Pd}(\text{CO})(\text{PPh}_3)_3$, $[\text{Pd}(\text{NH}_3)_4]\text{Cl}_2$, and $\text{Pd}(\text{C}_2\text{H}_4)(\text{PPh}_3)_2$, or mixtures of palladium with compounds generated by these complexes in the reaction system. Of these substances, organic acid palladium salts are preferred, with palladium acetate being particularly desirable. The amount of palladium component that is used in the reaction is in the range of 10^{-6} to 1 in terms of the mole ratio with respect to the aromatic hydroxy compound is desirable, with a range of 10^{-5} to 10^{-1} being particularly desirable.

[0010]

(B) Redox agent

The redox agent used in the present invention comprises a compound that contains cerium, cobalt or manganese metal ions. Trivalent and tetravalent cerium compounds can be used as the compound containing cerium ions, and examples include cerium chloride, cerium bromide, cerium sulfate, cerium nitrate and their inorganic salts; and cerium acetate, cerium oxalate and other organic acid salts. In addition, other examples include cerium acetylacetonate, cerium complexes formed by the coordination of such substances as carbon monoxide, nitriles, amines, phosphines or olefins on cerium, and mixtures of cerium and compounds generated by these complexes in the reaction system. Examples of compounds containing cobalt ions include divalent or trivalent cobalt compounds, for example, cobalt

chloride, cobalt bromide and other inorganic salts; cobalt acetate, cobalt formate, cobalt oxalate and other organic acid salts; and complexes with amines, ketones or carbon monoxide. Examples of compounds that contain manganese ions include divalent or trivalent manganese compounds, for example, manganese chloride, manganese bromide and other inorganic salts; manganese acetate, manganese formate, manganese oxalate and other organic acid salts; and complexes with amines, ketones or carbon monoxide.

[0011]

The amount of the aforementioned redox agent that is used in the reaction has no particular restrictions, but is preferably a mole ratio in the range of 10^{-3} to 10^2 with respect to the palladium component (A), with a range of 10^{-2} to 10 being particularly desirable.

[0012]

(C) Inorganic halide

The halide that is used in the present invention is an alkali metal or alkaline earth metal halide. Examples of preferable halides include chloride and bromides, such as lithium chloride, cesium chloride, sodium bromide, potassium bromide, rubidium bromide, cesium bromide and barium bromide. Of these substances, cesium chloride, and cesium bromide are particularly desirable. There are no particular restrictions on the amount of inorganic halide that is used in the present invention, but a

mole ratio in the range of 10^{-2} to 10^3 with respect to the palladium component (A) is preferred, with a range of 10^{-1} to 10^2 being particularly desirable.

[0013]

(D) Activated carbon

The activated carbon that is used in the present invention can be a commercially available substance, and the raw materials that can be used include wood, coconut husk, coal and pitch systems. The amount of activated carbon that is used in the reaction is 20x by weight or greater with respect to the palladium metal, with a range of 50-150x by weight being preferred.

[0014]

3. Reaction conditions

The reaction is performed by introducing the aforementioned aromatic hydroxy compound and catalyst comprising the aforementioned components (A), (B), (C) and (D) into the reactor, pressurizing the system with carbon monoxide and oxygen, and carrying out the reaction while heating. The reaction pressure is 10^{-2} to 50 MPa, with 10^{-1} to 25 MPa being preferred. From the standpoint of safety, it is preferable for the compositional ratio of carbon monoxide and oxygen to be outside the combustion range. The reaction temperature is in the range of 20-300°C, with 60-250°C being preferred, and 80-130°C being additionally

desirable. The reaction time is a few minutes to few hours. It is also effective to add a desiccant such as a molecular sieve to the reaction system, or to carry out the reaction while removing the water that is generated from the reaction system. Examples of solvents that can be used in the reaction include hexane, heptane, cyclohexane, benzene, toluene, xylene, methylene chloride, chloroform, chlorobenzene, diethyl ether, diphenyl ether, tetrahydrofuran, dioxane, ethyl acetate, methyl formate, acetonitrile and other inert solvents. There are cases where the raw material aromatic hydroxy compound serves as the reaction solvent, and it is not particularly necessary to use another solvent in such cases.

[0015]

Application examples

The present invention is described in detail below by providing application examples and comparative examples.

Application Example 1

3.0 g (32 mmol) of phenol, 2.7 mg (0.012 mmol Pd) of palladium acetate, 4.1 mg (0.012 mmol) of cesium (III)-chloride monohydrate, 40 mg (0.238 mmol) of cesium chloride and 100 mg of activated carbon (C/Pd = 77 weight ratio, Maruko P, manufactured by Nimura Kagaku Kogyo) were introduced into a Hastelloy autoclave with a volume of 30 mL. The interior of the system was replaced with carbon monoxide, and carbon monoxide was introduced at 6 MPa, while dry air was introduced at 3 MPa. The reaction was

carried out for 3 h at 100°C, and the reaction solution was then analyzed by gas chromatography. Diphenyl carbonate was obtained at a yield of 16.46% (2.63 mmol). In addition, phenyl salicylate was obtained as by-product at 0.35% (0.056 mmol), and p-phenoxyphenol was produced at 0.29% (0.046 mmol).

[0016]

Application Example 2

A reaction was carried out in the same manner as in Application Example 1, with the exception that the used amount of activated carbon was changed to 130 mg (C/Pd = 100, weight ratio). Diphenyl carbonate was obtained at a yield of 17.43% (2.79 mmol).

[0017]

Application Example 3

A reaction was carried out in the same manner as in Application Example 1, with the exception that the type of activated carbon was changed to Diahope ground product manufactured by Mitsubishi Kasei. Diphenyl carbonate was obtained at a yield of 13.64% (2.18 mmol).

[0018]

Comparative Example 1

3.0 g (32 mmol) of phenol, 2.76 mg (0.012 mmol Pd) of palladium acetate, 4.1 mg (0.012 mmol) of cerium(III)·acetate monohydrate and 40 mg (0.238 mmol) of cesium chloride were introduced into a Hastelloy autoclave with a volume of 30 mL. The interior of the system was replaced with carbon monoxide, and carbon monoxide was introduced at 6 MPa, while dry air was introduced at 3 MPa. The reaction was carried out for 3 h at 100°C, and the reaction solution was then analyzed by gas chromatography. Diphenyl carbonate was obtained at a yield of 4.22% (0.68 mmol). In addition, phenyl salicylate was obtained as by-product at 0.26% (0.042 mmol), and p-phenoxyphenol was produced at 0.46% (0.074 mmol).

[0019]

Effect of the invention

As is clear from the results presented above, the catalyst system of the present invention has high industrial value because it controls the production of by-products that are difficult to separate by distillation.

Japanese Kokai Patent Application No. Hei 8[1996]-89810

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